NITROGEN LOSSES IN RICE SOILS

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Abstract

A review is made of the recent work on nitrogen losses in rice soils. The topics covered include. denitrification, ammonia volatilization and losses due to leaching and
tion by soil minerals and soil org
portant processes for nitrogen losses
for the better quantification of nitrogen losses using ^{15}N labeled fertilisers under field
The prospects of improving the efficiency of fertiliser nitrogen have also been briefly discussed.

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Introduction

Fertiliser nitrogen applied to soils undergoes numerous physical, chemical and biological transformations (Fig. 1) which affect its loss and ultimate use efficien for crop production. The recovery of fertiliser nitrogen for rice is frustratingly low (Table 1) and is deterrent to getting the full potential yields from the modern high yielding varieties.

The main aim of search both in the developed and the developing countries is oriented towards enhancing the efficiency of fertilisers. This is not only essential for increased food production but also at the same time minimizes the ecological stress on the environment especially with regard to pollution of ground and surface waters. The study of fertiliser nitrogen transformations in soils is an important component of research for increasing the efficiency of nitrogen and undoubtedly better understanding of the various mechanisms of nitrogen loss will help in devising techniques for plugging these losses.

The main pathways of nitrogen loss in soils include the following:

1. Denitrification
2. Ammonia volatilization losses from ammonium and ammonium forming fertilisers.
3. Leaching and run off losses.
4. Chemical fixation and retention of ammonium clay minerals and amorphous materials.
5. Immobilization of nitrogen by soil micro-organisms.

It should be pointed at the outset that mentioned, viz., chemical fixation of ammonium and immobilization of nitrogen by micro-organisms are often temporary and may be considered as mechanisms of temporary loss of nitrogen but could be very important from the plant nutrition point of view particularly on short term basis.

The main objective of this paper is to review the recent literature on the various processes of nitrogen loss especially under rice soils. However, occasional examples have been cited from upland soils also, where data is scanty on rice soils.

Nitrogen Losses through Denitrification

The profile of a waterlogged soil is characterized by two distinct layers: (1) surface oxidized layer, generally of few mm to a cm thickness, present at the soil-water interface, (2) the reduced layer underlying. The surface layer corresponds to an oxidized zone where micro-organisms live aerobically. In the reduced layer anaerobic micro-organisms are found. But the rhizosphere of rice roots have changed conditions again and the soil particles associated with the rice roots are believed to be distinctly oxidized and represent a condition similar to the surface oxidized zone (67).

Perhaps, Shiori were the first to realise the importance of profile differentiation in waterlogged soils and observed considerable losses of from applied ammonium sulphate as the period of incubation proceeded. The losses of N were actually too great to be accounted for by volatilization or other mechanisms of loss known. They further observed that stirring had an effect, which helped in nitrifi tion of ammonium nitrogen. They felt that the N applied dized surface layer was nitrified and it moved down into the anaerobic zone possibly with soil percolate or by diffusion and got denitrified biologically and possibly chemically to gaseous nitrogen. This process has been subsequently confirmed by many researchers (20, 67, 81, 108). Broadbent and Tusneem (20) reported using ^{15}N that substantial losses of nitrogen occurred under flooded conditions in all cases except when NH_4^+ —N was rapidly immobilized and or fixed by clay minerals. They found that nitrification-denitrification was the mechanism excluded, there was no loss of N because there was no nitrate

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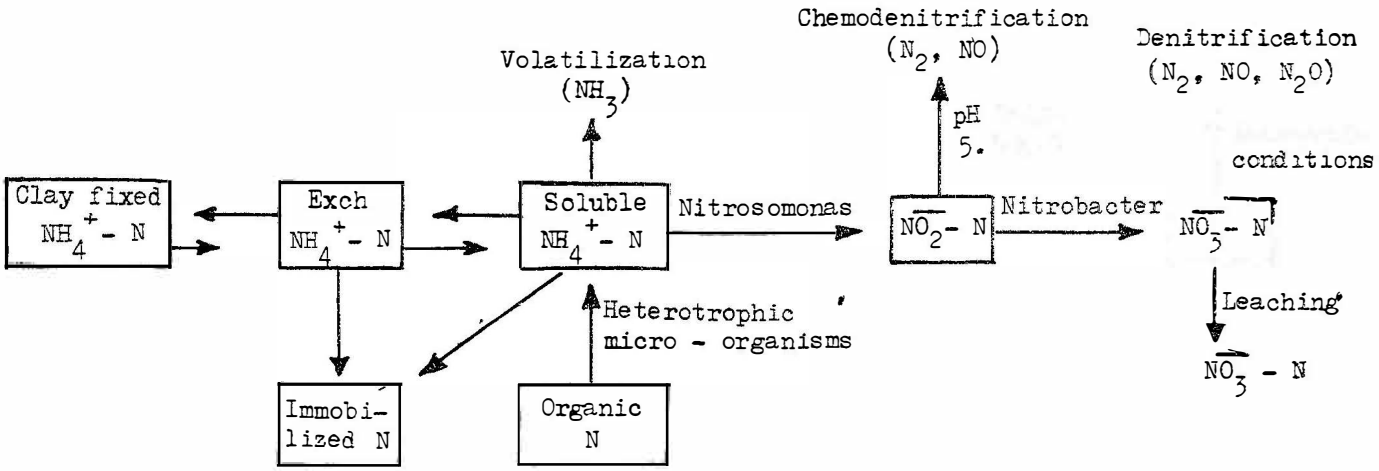

Figure 1—Nitrogen transformations in soils

formation and no N_2 was evolved. Their study provided a direct evidence for loss of N by nitrification-denitrification. There have been studies throughout the world indicating that these losses of N through nitrification and denitrification largely account for the low recovery of ammonium fertilisers by rice in the submerged soils (48). In India, Abichandani Patnaik (1) estimated these losses to range from 20 to 40 per cent while in Japan an estimate of 30 to 50 per cent loss of the applied N was made by Mitsui (67). Tusneem (117) measured losses from flooded soils using ^{15}N and reported as high as 68 per cent of the added nitrogen. In another study using ^{15}N-tagged ammonium nitrogen, Manzano (61) reported 37 per cent loss of N even with a rice crop growing on the soil.

Mitsui and Ota (68) in a tracer study of nitrogen transformation observed more losses of applied NH_4 air-dried soil and then flooded than when the application was made direct to undried soil. Takijima (114) reported the losses of nitrogen during flooded incubation conditions in the following order: Urea-N, NO_3^-—N, NH_4^+ —N. The cause of loss of

tion by alkaline reaction of the soil, while NO_3^- and NH_4^+ were lost mainly through denitrification.

It has been observed that nitrification and denitrification could proceed simultaneously in soils possibly due to the presence of aerobic and anaerobic microzones due to trapped oxygen of the air (42). In a tracer study of N transformation under waterlogged Patnaik (76) could not account for 23-24 per cent of the applied N at the end of the incubation. He attributed this loss of N to oxidation of ammonium to nitrate nitrogen in the surface layer of soil with subsequent leaching or diffusion and denitrification in the reduced zone. Similarly, using ^{15}N, investigations showed considerable losses of applied ammonium nitrogen due to denitrification after about four weeks of incubation (50).

Patrick and Wyatt (80) reported large losses of nitrogen as high as about 20 per cent of the total nitrogen or 400 lbs per acre as a result of several drying and flooding cycles. The major portion of this loss occurred during the first two or three cycles. These studies provide an indirect evidence of loss of nitrogen due to nitrification-denitrification. The losses resulted in reduction in yield and uptake of nitrogen by the rice crop under both greenhouse as well as field experimental conditions (79).

Manguiat and Yoshida (60) studied the nitrogen transformations of ammonium sulphate and alanine in submerged soil using ^{15}N tracer and reported that after 8 weeks of incubation, 25 and 22 per cent, respectively of nitrogen from ammonium sulphate and alanine was recovered in the soil. The nitrogen was lost rapidly from the soil when added either in organic or inorganic form. The loss could not be accounted for by volatilization or immobilization and was attributed to nitrification and subsequent denitrification during the incubation period. Presubmerged soils pro-

Table 1—Recovery of applied nitrogen by rice crop

Country	N applied (kg/ha)	N recovery (per cent)	References
1. USA	40—120	33-53	Westfall (1969)
2. Louisiana, USA	100 $^{15}(NH_4)_2SO_4$	33-61	Reddy and Patrick (1976)
3. India	120 $^{15}(NH_4)_2SO_4$	11-27	Upadhya et al. (1974)
4. Philippines	30 and 90 in rainy and dry seasons respectively	33 & 57 respectively	Racho and De Datta (1968)
5. Peru	180, urea	10-30	Sanchez and Calderon (1971)
6. India	100, labelled $(NH_4)_2SO_4$ and urea	18-38	Khind and Datta (1975)

vided a more favourable environment for nitrification than for denitrification under the experimental conditions.

The Soil Microbioiogy group at International Rice Research Institute, Philippines (50), also studied the fate of applied soils with a view to the movement of inorganic nitrogen into the organic fractions of soil N and its subsequent release. The most important organic N fractions in terms of immobilization were hydrolyzed NH_4^+—N fraction, amino acid fraction and amino sugars. N entering the exchangeable NH_4^+—N fraction following flooding was largely rived from hydrolyzed NH_4^+—N, amino acids—N and amino sugar—N fractions. An important feature of the study was that a considerable portion of the applied N was not accounted for in any of tions isolated. Losses of this N through nitrification and subsequent denitrification were speculated.

Nitrogen recovery results, using tracer techniques in greenhouse exper and discussed by Allison (5). The nitrogen fertiliser recovery from these experiments conducted under almost ideal conditions were reported to be between 80 and 90 per cent. In most cases, however, the lower recoveries were attributed to denitrification losses. Broadbent and Clark (16) have proposed four possible pathways for chemical denitrification in soils.

(i) Chemical decomposition of nitrous acid at low pH values resulting in loss of N as N_2.

(ii) Reactions of nitrous acids mith ammonia or urea.

(iii) Reactions between nitrous acids and α—amino acids.

(iv) Reactions of nitrous acids with other soil constituents like clay minerals, etc.

Racho and De Datta (86) using different rates of N application under flooded field conditions obtained a recovery ranging from 15 to 60 per cent during the dry season; however, during the wet season, the recovery was 15 to 35 per cent. It was further observed that the amount of nitrogen unaccounted for increased with the increasing rates of fertiliser N application.

The work done at IRRI has been recently summarized and discussed, which brings out that among the processes the loss of nitrogen in ammonia volatilization, nitrification-denitrification, leaching and immobilization are the most important and are responsible recovery of applied gen (28).

Severe losses of fertiliser nitrogen have been reported under fluctuating moisture conditions. Patrick and Tusneem (78) reported that an appreciable loss of labelled nitrogen occurred in flooded soils exposed to atmospheric oxygen and nitrog as ammonium was apparently nitrified in the aerobic surface layer and then diffused downward into the anaerobic zone where it was denitrified and lost from the system. The results of this study also show that losses of nitrogen can occur not only under alternate wetting and drying but also under continuously flooded soils mainly due to nitrification-denitrification. These losses in flooded soils will be determined by the concentration of atmospheric oxygen over a flooded soil. Nitrogen loss has been ness of aerobic governed by the amount of oxygen in the air (77).

Reddy and Patrick (89) reported that the rate of decomposition of organic matter was faster under treatments with the maximum number of cycles with alternate aerobic and anaerobic period. But there were heavy losses of total N (native and applied) as well as of the applied $^{15}NH_4$—N nitrogen. N losses as high as 24.3 per cent and 63.0 per cent of applied $^{15}NH_4$ resulted from the shortest (2 and 2 day) aerobic and anaerobic incubation. More nitrogen would possibly immobilization of part of the added ammonium N by added rice straw. Prasad and Rajale (84) also observed that urea nitrogen was rapidly lost under alternate wetting and drying though it was well conserved at field capacity and continuously flooded conditions in a laboratory study with a sandy clay loam soil. These authors found that the denitrification losses were reduced with inhibitors of nitrification and with slow release fertilisers like oxamide, IBDU and SCU. Recent studies at IRRI, ever, have shown that the nitrification-denitrification losses due alternate flooding and drying may not appreciably affect N uptake and growth of rice in soils unfertilised with N. But with high rates of N, there were significant decreases in N uptake and yield of rice (93).

There are many reports about the low efficiency of applied nitrogen under flooded rice soils. Westfall (125) estimated that in the United States rice areas, the fertiliser recovery ranges from 33 to 53 per cent with the rates of 40 to 120 kg N/ha. Racho and De Datta (86) reported a maximum efficiency of 33 per cent for application of 30 kg N/ha in the wet season and 57 per cent with the rate of 90 kg N/ha in the dry season in the Philippines. These out great losses of N under flooded rice soil conditions though these authors have not evaluated in detail the mechanisms of N loss although it is assumed that denitrification, leaching and immobilization are the most important processes involved. Reviews of De Datta and Magnaye (27) and Sanchez (104) bring out that the losses of applied nitrogen under flooded conditions are quite and these result in lower efficiency under tropical rice Tracer studies using ^{15}N-labelled fertil of mineral nitrogen occurred incubation test under flooded conditions. About 85 per cent of the total loss from the applied N occurred during the first two months. At the end of the four-month incubation period. about 68 per cent of the applied N was lost non-straw treatment as compared to about 43 per cent in the presence of added straw (2500 ppm C). Large scale losses (14 to 16 per cent) of the total curred under successive flooding and drying and above per cent of during the first two cycles of flooding and drying. There was greater mineralization of soil organic mat-

ter under fluctuating moisture
gimes resulting in greater loss of
both fertiliser as well soil nitrogen-
At the end of experiment, how-
ever, there was no difference in
mineral nitrogen content in the
presence or absence of straw,
which indicated that the less loss
of nitrog
by immobilization of
nitrogen (118). These authors also
observed that the remineralization
of immobilized labelled nitrogen
was in general slow. The most im-
portant organic forms were amino
acid N, hydrolyzed NH_4—N and
amino sugar N and accounted for
about 90 per cent of t
lized labelled N under waterlogged,
o
Nitrogen loss und
conditions was very likely caused
by nitrification of ammonium nitro-
gen at the oxidized surface layer
and subsequent diffusion and de-
nitrification loss of the nitrified
nitrogen in the anaerobic reduced
zone. The dissolved nitrate nitrogen
can enter the anaerobic zones
either by mass flow or diffusion
and is rapidly denitrified (83).
These losses will be controlled by
the oxygen diffusion rates int
upper layer of submer
thickness of the oxidized layer
and redox potential
have been discussed in details by
Ponnamperuma (83). Rennie and
Fried (92) observed a close rela-
tionship between N loss from
N
flooded soil measured at the sur-
face or at 10 cm depth in a green
house experiment.

Reddy et
and evaluated the major processes
controlling
soil under
It was observed that NH_4^+—diffu-
sion, nitrification, NO_3^- diffusion
and denitrification all occurred se-
quently in a flooded soil using la-
belled N. Under the conditions
of the experiment these pr
accounted for a loss
cent of the 200 ug $^{15}NH_4^+$—N per g
of soil initially applied after incu-
bation period of 60 days.

There are reports indicating that
large amounts of nitrate are lost
from air-dry soils when these
are flooded. Amounts as
as 500 ppm NO_3—N in the
soil solution or 700 kg/ha on a
soil basis may be lost within weeks
of flooding in a soil due to deni-
trification. This rapid disappear-
ance of NO_3—N may result in 20-
700 kg N/ha loss depending upon
the soil, cropping history, water re-
gime, etc., prior to flooding (49,
51). These losses can
high as revealed by the study at
the International Rice
Institute in which soil samples
from 280 lowland rice fields in the
Philippines were collected shortly
after harvest to study the loss o
nitrates during alternate
flooding. The nitrate content va-
ried from 5 to 39 ppm with a
mean of
when the soil is flooded and may
account for a lar
gen due to denitrification alone
(52). There are numerous reports
which highlight denitrification los-
ses in submerged soils (14, 15,
26, 59, 60, 82, 83, 113, 127, 129).

Losses through Ammonia Volatilization

A part of NH_4^+ or NH_4^+ form-
ing fertilisers could be lost through
NH_3 volatilization from a soil-water
system if the pH of soil or flood
water is high. Fertilisers like
can provide their own alkalinity
for this mechanism of loss due to
its hydrolyses to $(NH_4)_2CO_3$ by soil
urease activity. In case of NH_4^+
fertilisers, external source of alka-
linity is important even for initiat-
ing N
of urea, this source of alkalinity is
needed to maintain NH_3 volatiliza-
tion because NH_3 volatilization pro-
duces equivalent acidity in the
system from which NH

$$NH_4^+ \rightarrow NH_3^+ + H^+$$

Among the various factors af-
fecting ammonia volatilization, pH
is the most important and is a
combined indicator of the alkali-
nity and acidity of the system,
which may be
rough idea about how
NH_3 could be maximally lost from
a system based on the NH_4^+—NH_3
equilibria as discussed below:
Other source of alkalinity and
bases have also been enumerated.

NH_4^+—NH_3 Equilibria in flooded systems of rice soils:

$$(NH_4)_2 SO_4 \rightarrow 2NH_4^+ + SO_4^-$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

$$Kb = \frac{(NH_4^+)\,(OH^-)}{(NH_3)\,(H_2O)\ \text{const.}} = 1.8 \times 10^-$$

since (H_2O) remains constant, therefore,

$$(NH_3) = \frac{(NH_4^+)\,(OH^-)}{1.8 \times 10^{-5}} \qquad (1)$$

Also, $pH + pOH = 14$ (2)

or $pOH = 14 - pH$ (3)

By putting the values of NH_4^+ applied at different pH values of the system soil or flood water, the amounts of NH_3 formed could be calculated and verified experimentally

e.g., if the pH of flood water is say 9 and if
is applied then the amount of NH

$$(NH_3) = \frac{100 \times 10^{-5}}{1.8 \times 10^{-5}} = \frac{100}{1.8} = 55 \text{ ppm}$$

Therefore, out of 100 ppm of NH_4^+ applied 55
the NH_3 gas form when applied to a system having pH 9.0. The loss of this NH_3 formed will be fur
governed by the factor like size of the canopy of the crop, tempera-
ture, and wind velocity and other weather variables. However, if the pH of the system receiving NH_4^+ ap
amout of NH_3 formed will be only 5.5 per cent, which could be lost by volatilization. But this is the effect of pH only and pH is con-
trolled by the concentration or supply of bases in the form of carbonates and bicarbonates.

It is thus clear from the results shown in Table 2 that the potential of loss due to ammonia volatiliza-
tion will be si
of the system is
and may be considerable if pH is above 8.0.

Table 2—Concentration of ammonia (NH_3) and ammonium (NH_4^+) in aqueous system at different pH values

pH	Per cent of applied NH_4^+	Ammonium as NH_3
5.0	99.9945	0.0055
6.0	99.9450	0.0550
7.0	99.4500	0.5500
8.0	94.5000	5.5000
9.0	45.0000	55.0000
10.0	—	>100

In addition to carbonates and bicarbontes, the other sources of alkalinity could be:

(a) Sulfate reduction, (b) iron reduction and (c) denitrification reactions, which generate alkalinity in form of bicarbonates or carbonates, which could be important for ammonia volatilization losses. Furthermore, growth of bioata like algae which use the CO_2 evolved from soils for photosynthesis may further raise the pH of the system.

The important factors that influence NH_3 volatilization from soil are pH, cation exchange capacity, exchangeable cation, texture, temperature, water content, the nature of NH_4 source and the rate and method of application. Many reports have emphasized the important role of pH on NH_3 volatilization (24, 30, 57, 58, 62, 94, 120). It has generally been observed that the higher the pH, the greater the NH_3 loss (24, 30, 120). Higher losses of NH_3 volatilization have been reported at higher temperatures (4, 12. 13, 32, 36, 123), lower cation exchange capacity (4, 38, 39, 62, 123) and high moisture loss (32, 57). Under flooded field conditions in addition to the above enumerated, the growth of algae on the surface of rice paddies can influence these losses to a greater extent by fixing the CO_2 and increase the pH of the surface water (13, 94). The losses from soils having higher content of $CaCO_3$ or alkalinity are known to be potential for ammonia volatilization (32, 34-39, 54, 123).

Some studies have suggested that there could be loss through NH_3 volatilization even in acid soils (12, 30, 58. 121) though the magnitude is quite small. The nature of N source also plays an important role in NH_3 losses (58, 63, 120). Larger losses have been observed with urea than with ammonium sulphate and slow release N sources (58, 63, 120). Many workers have concluded that placement of NH_4^+ sources in soils considerably reduced the NH_3 volatilization losses with all N sources (39, 58, 105, 120). Shankeracharya and Mehta (105) studied NH_3 volatilization losses under laboratory conditions with some Indian soils using air-flow technique. Effects of various factors like moisture, rate of N, soil pH, temperature, soil texture, sterilization flooding, source of N and depth of placement on volatilization losses were studied. The loss in loamy sand soils were 58 per cent at 15 per cent WHC moisture and 34 per cent at 75 per cent WHC from surface applied—urea at the rate of 440 KG N/ha in 14 days in the hot month of May. These losses were found to increase with increase in pH, temperature and rate of N application. Soil sterilization was not effective in reducing the loss. The order of loss from different N carriers was urea > groundnut cake > ammoniacal forms. It was significant to note that the losses were practically negligible when urea was applied 5 cm deep in the soil. the losses were considerably reduced if at least 2.5 cm of water was given immediately after the application of urea.

In another report on the losses due to volatilization of NH_3 from salt affected Indian soils, Gandhi and Paliwal (41) concluded that losses increased with increase in salinity and were about 35 $\pm$ 5 per cent of added N (250 and 500 ppm of $(NH_4)_2SO_4$ and urea) at an Ece of 45 to 50 m mhos/cm. Salinity and pH both were positively correlated with the volatilization loss of NH_3 in these salt affected soils

Denmead Frency and Simpson (29) in an interesting study on NH_3 losses from a grass-clover pasture in Australia, using combined chemical micrometeorological technique reported that losses of NH_3 from grazed pasture were quite considerable ($\sim$ 13g $ha^{-1}h^{-1}$) However, the extent of losses from the ungrazed pasture were relatively small ($\sim$ 2g N $ha^{-1}h^{-1}$). These workers further pointed out that though there were large amounts of NH_3 produced near the ground within canopy but there was almost complete absorption of NH_3 by the plant cover. The amounts of NH_3 absorbed appeared to be too large for stomatal uptake alone. This study clearly points out the importance of canopy of plants which has a closed NH_3 cycle going on and this has important consequences for the field assessment of N fixation ad gaseous N losses It thus should be recognised that though there can be NH_3 volatilized from the soil surface but if there is plant canopy, siderably reduce the losses of NH_3 volatilized by absorbing it.

There have been few studies about NH_3 volatilization losses under flooded soil conditions and the data on ammonia volatilization is summarised in Table 3. Gupta (43) reported that 22 per cent of the surface applied 66 kg N/ha as ammonium sulphate to an alkaline wetland soil (pH 8.4) was lost due to ammonia volatilization in a laboratory study. At the International Rice Research Institute in a laboratory study Mac Rae and Ancajas (58) studied ammonia volatilization losses in soils varying in pH (3.6-8.1), organic matter (2.0-10.0 per cent) and CEC (23 to 54 m.e./100 g of soil) for 7 weeks. Calculations of NH_3 ses from their data shows that the maximum losses with $(NH_4)_2SO_4$ were around 7 per cent while with urea it was as high as 19 per cent of the applied N (50 and 200 kg N/ha) within 7 weeks. Their study showed some detectable losses occurred even in an acid sulfate soil (around 0.3 to 0.4 per cent). The extent of NH_3 loss was considerably reduced when the N was placed and incorporated. Bouldin and Alimagno (13) studied the losses due to ammonia volatilization under field conditions employing an open-closed bottle systems. The measurement of losses was done indirectly by difference between closed and open bottles with broadcast application of $(NH_4)_2SO_4$ and urea N at rates varying from 40-60 kg N/ha. Their study thus allowed the natural turbulance of air responsible for NH_3 sweeping away which was the major difference between other studies carried out in laboratory or greenhouse or even in the field where losses were measured using H_2SO_4 sink in a closed system allowing no turbulence of air to the water-atmosphere interface. Also this study under field conditions was affected by factors like algal growth temperature and sunshine which directly or indirectly influence immensely NH_3 volatilization. These workers reported NH_3 losses in the range of 30-60 per cent of the applied NH_4^+ within 3-5 days after N application.

Table 3—Ammonia volatilization losses from flooded rice soils

Sl. No.	Soil	Kind of study	Fertiliser	N rate kg/ha	N loss per cent	References and remarks
1.	Crowley silt loam	Laboratory	Urea	112-448	5-10	De Laune and Patrick (1970). air flow technique with boric acid as sink.
2.	Flooded soil	Laboratory	$(NH_4)_2SO_4$, urea	50 & 200	0.5-7.0	Mac Rae and Ancajas (1970), H_2SO_4 used as sink for NH_3 absorption.
3.	Flooded alkaline soil (pH 8.4)	Laboratory	$(NH_4)_2SO_4$	66	22	Gupta (1955).
4.	Maahas clay (pH 7.0-8.4)	Greenhouse	$(NH_4)_2SO_4$	100	1-16.5	Ventura and Yoshida (1977), H_2SO_4 used as sink for NH_3 absorption.
		Field	$(NH_4)_2SO_4$ and urea	100 100	3.3-4.0 1.5-8.0	
5.	Maahas clay	Field	$(NH_4)_2SO_4$	40-60	30-60	Bouldin and Alimagno (1976) used open and closed bottle system.
6.	Flooded Philippine soils	Tanks in field	$(NH_4)_2SO_4$	100	6-49%	Sahrawat (1978), used open and closed bottle system.
7.	Maahas clay and Luisiana clay	Greenhouse	$(NH_4)_2SO_4$	30-90	0.01-5.8	Mikkelsen et al (1978), constant air-exchange using H_2SO_4 trap.
		Field	$(NH_4)_2SO_4$, urea	30-90	0.25-20	

Ventura and Yoshida (120) measured NH_3 volatilization losses from different N fertilisers from Mashas clay under greenhouse and field conditions. They reported that NH_3 losses occurred during the first 9 days after N application. The losses were very small when the soil pH was below 7.5 but increased with the increase in pH of the soil. Direct field measurement showed that about 3.8 per cent of N was lost from broadcast application of 100 kg N/ha as $(NH_4)_2SO_4$ but these losses amounted to 8.2 per cent for urea during 21 days. In greenhouse, with soil pH 8.1 NH_3 volatilization losses were around 17 per cent. These losses reduced by about 50 per cent when the fertiliser materials were incorporated in the puddled soil. Sahrawat (94) studied ammonium volatilization losses in four lowland rice soils of the Philippines and reported that the losses of surface applied ammonium sulfate were least (6 per cent) in an acid soil and the highest (50 per cent) in alkalized clay. Further a striking relationship in the pH chan and the losses through ammonia volatilization was observed in the pH of the flood water of these soils, i.e., higher the pH of the flood water higher the ammonia loss and ammonia volatilization losses.

The review of literature bring out that NH_3 volatilization losses could be significant under soils with high pH (calcareous or sodic soils), with low cation exchange capacity and under high temperature conditions prevalent in tropics. However, lack of data on the subject for flooded soils makes it difficult to draw any plausible conclusions. But it has been amply recognized that placement and incorporation of NH_4^+ can significantly reduce losses due to NH_3 volatilization. Another interesting aspect seems to be the canopy of crop, which may at least reduce the NH_3 volatilization losses by entrapping a part of the NH_3 volatilized. Under field conditions, growth of algae, wind speed and the diurnal changes in pH due to biological respiration and CO_2 fixation will be very important, which may be probably fully ignored in a laboratory and partially under greenhouse experimental

Losses due to Leaching, Surface Run off

There is lack of scientific data on this aspect of N losses in soils particularly in rice soils. However, there are indications that in light textured soils under poor control of water, a part of NH_4^+ or NO_3^- could be lost by leaching or even in surface run off.

Studies carried out in Japan estimates an average loss of about 20 kg N/ha every year through leaching from rice fields (128). Similarly, Koshino (56) concluded from the review of the literature on field lysimeter studies conducted during the past 50 years in Japan that the leaching losses ranged from 3 to 25 per cent of the applied fertiliser nitrogen. In India, Pande and Adak (75) reported that in paddy soils, the losses due to leaching could be from 45-60 per cent from the basal application but these losses were reduced to 11-33 per cent from split application of nitrogen.

Fixation and Retention of Ammonium by Soil Clay Minerals and Amorphous Soil Materials

It has been observed by many workers that in some soils quantitative recovery of added NH_4^+ could not be obtained, even when soils were extracted immediately after addition of NH_3^+. Such ob-

servations have been made by many workers starting from the pioneering study of Mc Beth (65) on ammonium fixation, in which it was concluded that various anions associated with NH_4^+ do not affect fixation, that fixation is greater at 100°C than at 5°C and that NH_4^+ retention or adsorption was due to clay fixation. Since then the phenomenon of NH_4^+ fixation has been observed and characterized by other researchers (19, 46, 112). It was concluded from these studies that some of the NH_4^+ is fixed so tightly that it was resistant to extraction even with prolonged boiling with 6N HCl. The tracer N recovery was invariably less than that of total NH_4^+. It has been shown by other workers since then that fixation is due to trapping of NH_4^+ ions within the crystal lattice of montmorillonite, vermiculite minerals and due to tie-up by soil organic matter (6, 8, 110).

Thus, it has been recognised that clay minerals can fix NH_4^+ which can be explained on the basis of entrapment of NH_4^+ ions resulting from contraction of the 2 : 1 lattice. However, there are some soils developed from volcanic ash in areas with high rainfalls, which predominantly have amorphous colloidal hydrated oxides of aluminum and iron and in some cases also as allophane, and these soils also fix NH_4^+ as shown by Tamiri et al (115) in Hawaiian soils. Because such soils adsorb high amounts of PO_4^{3-} and NH_4 forms products like taranakite $(NH_4)_2 H PO_4$ as a reaction product. which may be responsible for NH_4^+ fixation in such soils. However, presence of Fe^{3+} Al^+, PO_4^{3+}, NH_4^+ and/or K^+ and moisture and an acid reaction are prerequisite for the formation of taranakite (11, 69, 122).

It has been found that among other factors which affect NH_4^+ retention or fixation with minerals and soils. pH, moisture content, clay mineral content and nature of minerals, organic matter and presence of cations like K^+ have been shown to be important by many workers (9, 18, 21, 23, 44, 106, 111).

There have been contradictory reports about NH_4 fixation in flooded vs upland soils. It has been postulated that there will be less immobilization of N under flooded conditions as compared to lower moisture conditions because the microorganisms work at a lower energy level. However, some workers have reported more retention of NH_4^+ under submerged conditions (106). There have been increasing relationships between fixation of K^+ and NH_4^+ when added to soils at different concentrations and order of applications (70, 71) and it has been concluded that the two cations are fixed in nearly equivalent proportions but NH_4^+ was fixed preferentially to K^+ when added together to soil. It seems from these that K fertilisation may be an important factor in the fixation and release of NH_4^+ in soils particularly on long term basis.

In a laboratory experiment, Raju and Mukhopadhyay (88) studied the influence of saturation of specific cations on NH_4^+ fixation in six Indian soils differing in physicochemical and mineralogical properties. It was found that the effects were in the following order: $Ba^{2+} > Na^+ > Ca^{2+} >$ control $> K^+$. Treatment with K^+ apparently removed some NH_4^+ fixed in soils prior to sampling. The NH_4^+ fixation was found to be correlated to the amount of clay present except in one soil. Recently, Feigin and Yaalon (33) have reported that in Israel soils, clay fraction was a significant factor influencing the amounts of non-exchangeable NH_4^+ in soils. The relatively low amounts of non exchangeable NH_4^+ found are consistent with the predominant clay mineral in most of the soils being montmorillonite. A good correlation was found with the content of illite, which is the main carrier of the non-exchangeable NH_4^+. Ayed and Bargseth (7) reported that the NH_4^+ added to illite, and kaolinite was best recovered by K. In vermirculite Na^+ was the superior extractant. In montmorillonite, however, K^+ recovered more of the added NH_4^+ than Na^+ when the extraction was performed prior to drying but the extracting power of the cations was reversed upon drying. Similar results were obtained with montmorillonitic soils. In a laboratory study with different Philippine soils of volcanic origin. Sahrawat (96) found that these soils fix NH_4^+ in a way that only up to 80-90 per cent NH_4^+ can be recovered after 2 hours of application to soil and K^+ was a better extractant for recovering NH_4^+ —N applied than Na^+. In a laboratory study, the ammonium fixing capacity of 12 Philippine rice soils were found to be related to the active iron content of soils but was not related to clay content, organic matter content and pH of soils. Perhaps, the iron oxides in combination with organic matter and allophonic materials seem the probable cause of ammonium fixation. This oxidation and reduction of iron compounds in these soils be important or adsorption and desorption of NH_4^+ (97).

The review of literature brings out that NH_4^+ can be fixed both by clay minerals as well amorphous materials in soils and may be rendered unextractable even after short time of application. The mechanism of fixation by these materials seems to be different but is not very clear from the work gathered. The data summarized in Table 4 shows that the amounts of naturally occurring fixed NH_4 may form a major portion of total N in some soils. It should be pointed that NH_4 fixation by soil materials may be only a temporary loss of N to plants but may ultimately go to the advantage in terms of its value in minimising losses due to nitrification-denitrification or by leaching because of non-availability of fixed NH_4^+ to microbial transformations. There are very few studies pertaining to the availability of fixed NH_4^+ to rice but some of the recent studies do point out that a great fraction of the fixed N is mineralized under flooded conditions and made available to rice plants (Personal communication, Prof. F. E. Broadbent 1977, University of California, Davis).

Immobilization

There is continuous interchange between organic nitrogen and inorganic forms of nitrogen in soils because of mineralization and immobilization processes going on

Table 4—Naturally occurring fixed ammonium in soils

Region	No. of samples studied	Amount of fixed NH_4^+ (ppm)	Fixed NH_4^+ per cent of total N	References
Wisconsin, USA	21	25-133	1 3-22.6	Walsh and Murdock (1960)
Nigeria	212	4-98	1-48	Obuwarib and Odu (1974)
Uttar Pradesh (India)	10	12-37	4-20	Singh and Dixit (1972)
West Bengal (India)	18	92-319	18-54	Raju and Mukhopadhyay (1974)
Israel	129	5-137	1.8-78.6	Feigin and Yaalon (1974)
New South Wales (Australia)	6	19-112	3-33	Osborne (1976)
Philippines	16	7-428	0.4-56.5	Tilo et al (1977)
Trinidad	3	365-1682	18.9-76.7	Dalal (1977)

continuously in soils. These processes are important from plant nutrition point of view because a major portion of soil nitrogen exists in organic form and only a small fraction of this minralizes in a growing season, which is available to plants. Also if organic materials with high C/N ratio are added to soils, there is a quick immobilization of inorganic nitrogen in building up of the cell materials of microorganisms and the inorganic nitrogen is blocked in the organic form. On the other hand, there is net mineralization if the residues added have a low C to N ratio.

According to Broadbent and Nakashima (18) and Williams et al (126). the immobilization effects due to straw application in soils depend on the quantity of straw applied, N content of straw and total N content of soil. It has been generally observed that the immobilization of soil or fertiliser N is always lower under flooded conditions compared to counterpart aerobic soils because under flooded situations bacteria are the main microorganisms, which operate at lower energy level and synthesize much less cell materials resulting in less net immobilization of nitrogen (2, 3, 18, 83).

Broadbent and Nakashima (18) observed that though the N factor or the additional N immobilized per unit weight of straw varied with the quantity of straw applied, N content of the straw and the nature of soluble N supplied but in no case it was negligible. It is thus recognized that though the decomposition of plant residues is faster under aerobic or upland soil conditions but because of the greater effects due to immobilization by soil microorganisms, the amounts of net mineralized nitrogen released are lower than in the flooded soils, where though the decomposition of the plant residues is slower but because of the less immobilization effects the net amounts of mineral nitrogen are always higher.

Another important factor to be considered in the mineralization-immobilization of nitrogen in soils is the content of total N of the soils. It has been generally accepted that the immobilization of soil or fertiliser nitrogen will be far less or none in a soil rich in nitrogen than in a nitrogen deficient soil. Sahrawat (unpublished report, 1978, IRRI, Philippines) reported that the rice straw, containing 0.50 per cent N added at the rate of 1,500 ppm of soil did not had any significant effect on the immobilization of soil or fertiliser nitrogen in three Philippine low land rice soils, when incubated under flooded conditions in the laboratory for 8 weeks.

The nitrogen factor, which is defined as the weight of nitrogen immobilized by 100 g of the decomposing residue (47) has been investigated by many researchers. Acharya (3) reported that the nitrogen factor for aerobic flooded and anaerobic conditions were 0.54, 0.39 and 0.07 respectively. Williams et al (126) reported no net immobilization of nitrogen if the incorporated rice straw in a flooded soil has nitrogen content of 0.50 per cent or higher. Broadbent and Nakashima (18) suggested a nitrogen factor of 0.51 with rice straw containing 0.47 per cent nitrogen, and a factor of 0.43 with immature rice straw containin 1.17 per cent nitrogen for a flooded soil.

Perspectives in Increasing the Efficiency of Fertiliser Nitrogen

The review of literature brings out that the recovery of fertiliser nitrogen by rice crop rarely exceeds 50 per cent under tropical agricultural conditions and among the mechanisms of loss the prominent ones usually are denitrification, ammonia volatilization and under specific situation losses due to leaching could be high but no data is available to substantiate this under field conditions.

The various approaches to minimize nitrogen losses include agronomic cultural practices involving split application of nitrogen at the growth stages requiring nitrogen and where it is utilized efficiently, time of application and the method of application also become quite important for efficient untilization of nitrogen. Another practice found attractive along with the proper timings of nitrogen application by many workers for minimising losses due to nitrification-denitrification and volatilization of ammonia is the placement of fertiliser nitrogen in the reduced soil zone. The results on yield and uptake of nitrogen by rice by using deep placement of nitrogen have been very encouraging (17, 28, 53, 90).

Another approach for making the efficient use of fertiliser N is by using slow release fertiliser materials so that the nitrogen re-

lease matches nitrogen uptake by plant. Certainly, this will result in reduced losses due to denitrification, ammonia volatilization and leaching and improved utilization by the crop (31, 85). Yet another attractive means of reducing nitrogen losses due to leaching and denitrification accompanying nitrification could be achieved by using chemicals called nitrification inhibitors. A large body of literature on the subject has been reviewed by Gasser (40), Prasad et al (85), Hauck (45) and Engelstad and Russel (31). Sahrawat (95) reviewing the literature on the use of nitrification inhibitors concluded that the use of these chemicals hold promise to improve the efficiency of nitrogen for crops under situations where severe losses due to denitrification and leaching are likely to occur. Use of some cheap and indigenous nitrification inhibitors may be the right approach to exploit these materials for increasing the efficiency of fertiliser nitrogen under situations where losses dut to denitrification and leaching are severe due to improper control of water. There is an obvious need to exploit the use of indigenous materials specific to local conditions for retarding nitrification of ammonium and ammonius forming fertilisers (98-102).

An attractive approach for making efficient use of urea fertiliser nitrogen is by retarding the rates of urea hydrolysis in soils by using chemicals called urease inhibitors. This approach may be helpful in reducing the losses due to ammonia volatilization and may alleviate ammonia toxicity to seeds and seedling plants (22, 64). However, the use of urease inhibitors may offset the advantages in lowland rice soils where the loss of urea due to leaching is high.

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